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浆果楝中的新木脂素

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摘要：从浆果楝（*Cipadessa baccifera*）中分离得到两个木脂素，其化学结构通过波谱方法鉴定为：(－)-9′-O-(E)-coumarate-5，5′-dimethoxylariciresinol（**1**）和（＋)-9′-O-(E)-feruloyl-5，5′-dimethoxylariciresinol（**2**）。其中化合物**1**为新化合物。

关键词：浆果楝；木脂素；(－)-9′-O-(E)-coumarate-5，5′-dimethoxylariciresinol

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Lignans from the Stem of *Cipadessa baccifera* (Meliaceae)

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Abstract：One new lignan，(－)-9′-O-(E)-coumarate-5，5′-dimethoxylariciresinol（**1**），together with one known compound，(＋)-9′-O-(E)-feruloyl-5，5′-dimethoxylariciresinol（**2**）was isolated from the stem of *Cipadessa baccifera*. The new structure was elucidated by spectroscopic methods.

Key words：*Cipadessa baccifera*；Lignan；(－)-9′-O-(E)-coumarate-5

Cipadessa baccifera (Roth.) Miq. (Meliaceae) is widely distributed in southwest of China and has been used in folk medicine for the treatment of rheum，dysentery，and pruritus. Previous efforts on this plant have reported a series of limonoids (Luo *et al.*，2000；Gan *et al.*，2007；Lin *et al.*，2008). As a part of our phytochemical investigation on plants in Meliaceae family，two lignans (**1**－**2**) were isolated from the stem of this plant (Fig. 1). Of them，**1** is a new compound. The known compound was determined to be (＋)-9′-O-(E)-feruloyl-5，5′-dimethoxylariciresinol (**2**)，by comparison of its NMR data with those in the literature (Chen *et al.*，2008).

Results

Compound **1** was isolated as white amorphous powder. Its molecular formula was established as $C_{31}H_{34}O_{10}$ according to the ion peak at *m/z* 589.2068 $[M+Na]^+$ on HR-ESIMS (calcd. for 589.2049). The presence of hydroxyl group in **1** was revealed by the strong absorption band at 3432 cm^{-1} in the IR spectrum. The ^{13}C NMR (DEPT) spectrum (Table 1) exhibited resonances for one methylene at δ 33.8 (t)，two methines at δ 42.7 (d) and 49.1 (d)，two oxygenated methylenes at δ 62.7 (t) and 72.7 (t)，one oxygen-bearing methine at δ 83.6 (d)，as well as several methoxy groups at δ 56.3 (q，

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overlapped) and a series of aromatic carbons. The above spectroscopic features indicated that **1** might be a lignan. A detailed comparison of the ^{1}H and ^{13}C NMR data of **1** with those of (+)-9′-O-(E)-feruloyl-5, 5′-dimethoxylariciresinol suggested that their structures were closely related (Chen *et al.*, 2008), except H-3″ [6.82, d (8.5)] of **1** replaced the 3″-OMe group. This was supported by the ^{1}H-^{1}H COSY correlations of H-2″/H-3″ (= H-5″/H-6″) and the apparent HMBC correlations between H-2″ and C-7″ (Fig. 2). The relative configuration of **1** was determined by ROESY spectrum. The observed correlations of H-7′/H-9′a and H-9′b suggested that H-7′ and H-8′ were on the opposite position and H-8′ was arbitrary assigned as β orientation. While H-8 was determined to be β orientation due to the presence of correlation of H-7′/H-7a. Thus, the relative configuration of **1** was fully established as shown (Fig. 3).

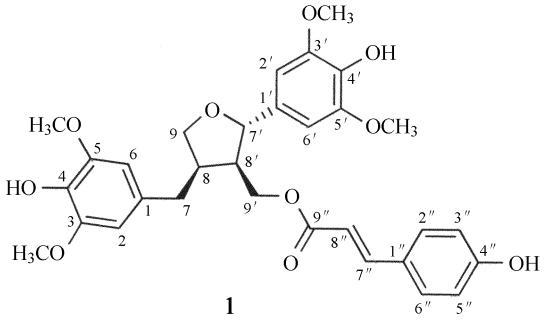

Fig. 2 COSY (—) and selected HMBC (→) correlations of 1

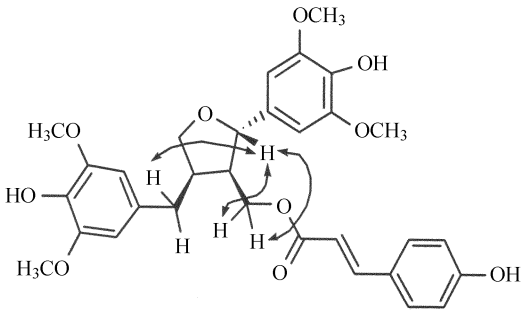

Fig. 3 Selected ROESY correlations (↷) of 1

1

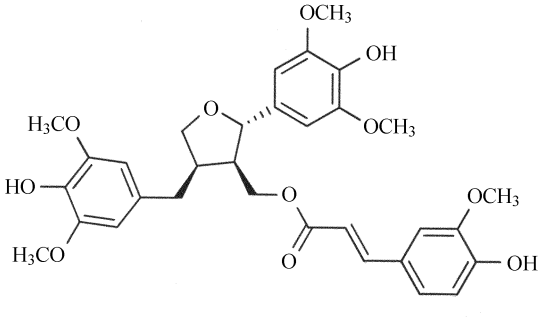

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Fig. 1 Lignans from the stem of *Cipadessa baccifera*

Experimental

General Experimental Procedures Optical rotations were determined with a Perkin-Elmer 241 polarimeter. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer with a KBr disk. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer, while 2D NMR spectra were recorded on and a Bruker DRX-500 instrument. ESIMS and HRESIMS spectra were measured with a Finnigan MAT 90 instrument and VG Auto Spec-3000 spectrometer, respectively. Semipreparative HPLC was performed on a Merck column (i. d. 100－10 mm; Merck, Darmstadt, Germany), developed with CH_3OH/H_2O (50∶50 to 58∶42, 35 min) (flow rate, 3.0 ml·min^{-1}, detection, UV 210 nm) at 30℃. Column chromatography was performed on silica gel (90－150 μm; Qingdao Marine Chemical Inc.), MCI gel (CHP20P, 75－150 μm, Mitsubishi Chemical Industries Ltd.), C18 reversed-phase silica gel (20－45 μm; Merck, Darmstadt, Germany), and Sephadex LH-20 (40－70 μm; Amersham Pharmacia Biotech AB, Uppsala, Sweden). TLC plates were precoated with silica gel GF_{254} and HF_{254} (Qingdao Haiyang Chemical Plant, Qingdao, People's Republic of China).

Plant material The stem of *C. baccifera* were collected in Xishuangbanna, Yunnan Province, People's Republic of China, and were identified by Prof. Jing-Yun Cui of the Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences.

Extraction and Isolation Air-dried stem bark *C. baccifera* (6.9 kg) was extracted three times with 95% EtOH. The extracts were combined and concentrated, then suspended in H_2O. The water layer was then extracted with ether (PE) and EtOAc. The EtOAc extracts (326 g) were subjected to silica gel column chromatograph, eluted with petroleum ether/Acetone (from 1 : 0 to 1 : 1), yielding 6 fractions A1-A6. Fraction A5 (16 g) was then subjected to C-18 column chromatograph (eluted with CH_3OH/ H_2O from 5 : 5 to 10 : 0), yielding 8 fractions B1-B5. Fraction B2 (1.5 g) was first purified on Sephdex LH-20, yielding three fractions C1-C3. Fraction C2 (210 mg) was subjected to silica gel, eluted with $CHCl_3$/acetone (10 : 1) to afford **1** (10 mg) and **2** (15 mg).

(+)-9′-O-(E)-coumarate-5, 5′-dimethoxylariciresinol (**1**): white amorphous powder, $[\alpha]_D^{25}$ +5.3 (*c* 0.4, MeOH); IR ν_{max}^{KBr} cm^{-1} 3432, 1629, 1174; positive-ion ESIMS *m/z* 589 $[M+Na]^+$; HR-ESIMS *m/z* 589.2068 $[M+Na]^+$, calcd 589.2049; ^1H NMR and ^{13}C NMR data, see Table 1.

Table 1 ^1H and ^{13}C NMR data of **1** in $CDCl_3$

No.	δ_H (mult, *J*)	δ_C	No.	δ_H (mult, *J*)	δ_C
1		131.1	6′	6.57, s	102.5
2	6.40, s	105.2	7′	4.81, d (6.5)	83.6
3		147.0	8′	2.65, t (6.5, 7.4)	49.1
4		133.1	9′a	4.33, dd (11.0, 3.5)	62.7
5		147.0	9′b	4.51, dd (11.0, 6.5)	
6	6.40, s	105.2	1″		126.7
7a	2.55, dd (11.0, 2.0)	33.8	2″	7.37, d (8.5)	130.0
7b	2.87, dd (11.0, 5.0)		3″	6.82, d (8.5)	115.9
8	2.75, m	42.7	4″		158.1
9α	3.77, dd (8.5, 1.5)	72.7	5″	6.82, d (8.5)	115.9
9β	4.08, dd (8.5, 6.5)		6″	7.37, d (8.5)	130.0
1′		133.4	7″	7.51, d (16.0)	145.1
2′	6.57, s	102.5	8″	6.23, d (16.0)	114.7
3′		147.0	9″		167.2
4′		134.0	OMe	3.85	56.3
5′		147.0			

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